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Evaluation of adsorbents for volatile methyl siloxanes sampling based on the determination of their breakthrough volume

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ABSTRACT

Volatile methyl siloxanes (VMS) have been detected in many different atmospheres such as biogas, sewage sludge, landfill gas, gasoline and ambient air. In these different atmospheres, their presence can involve several contamination problems and negative effects in industrial processes, their identification and quantification become a real challenge. Up to now there is no standardized procedure for VMS quantification, the sampling step remaining the major obstacle. Sampling gas through sorbent tube followed by analysis on TD-GC–MS is one of the reliable possibilities. It gathers sampling and preconcentration in one step and allows discrimination between all VMS, despite the difficulty to choose the appropriate adsorbent in order to avoid loss of analytes during sampling. In this context, this work deals with the comparison of different types of adsorbents based on the determination of the VMS breakthrough volume (BV). Although Tenax TA is the most widely used adsorbent, experiments show low BV values for the lightest VMS. At 25 °C, the BV of TMS and L2 are, respectively, 0.2 and 0.44 L g^{-1} which can contribute to an underestimation in concentration during their quantification. Carbosieve SIII usually used for C2–C5, did not adsorb light VMS as it was expected, and breakthrough volume obtained for VMS are more than ten times less than the values obtained for Tenax. On other hand, Chromosorb 106 and Carboxen 1000 in association with Carbotrap C and Carbotrap proved to be appropriated for VMS sampling, due to the high breakthrough volumes obtained for the lightest compounds comparing to the other adsorbents. The BVs of TMS for Carboxen 1000 and Chromosorb 106 are 1.2×10^4 and 39 L g^{-1}, respectively, and 49×10^4 and 1142 L g^{-1} for L2, respectively.

1. Introduction

VMS are a man-made chemical family containing silicon, oxygen and methyl groups. Their structure can be either linear (L) or cyclic (D). VMS are widely used in various industrial processes [1–3] and are frequently added to consumer products, such as detergents, shampoos, cosmetics, paper coatings and textiles. They are, moreover, released as a residue in production of silicon containing chemicals [4,5]. Due to their widespread use, they can be found in wastewater treatment plants, biogas etc. Table 1 lists some typical VMS and some of their properties.

Recently, there have been extensive reviews assessing the environmental risks of VMS as potential priority pollutants in Europe [6,7], in Canada [8,9] and similar assessments have been completed or are underway in the United States [10]. For example recently the Canadian government has released assessment reports on octamethylcyclotetrasiloxane D4 and decamethylcyclopentasiloxane D5 and recommended to add (D4) and (D5) to the list of toxic substances. They may have an immediate or long-term harmful effect on the environment or its biological diversity [8,9].

Because of wide use of VMS, they have been detected in many different atmospheres such as, biogas, sewage sludge, landfill gas, gasoline and ambient air [11,12]. In these different media, their presence can involve several contamination and operational problems. For example, during combustion of biogas they are transformed into hard solid silica which is very abrasive and can

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Table 1
The most common VMS and their properties [3,5,8].

Compound	Abbreviation	Molar mass ($g\ mol^{-1}$)	Water solubility at 25 °C ($mg.l^{-1}$)	Boiling point (°C)
Trimethyl silanol	TMS	90	3.5×10^{4}	70
Hexamethyldisiloxane	L2	162	9.3×10^{-1}	107
Octamethyltrisiloxane	L3	236	3.5×10^{-2}	153
Decamethyltetrasiloxane	L4	310	6.7×10^{-3}	194
Dodecamethylpentasiloxane	L5	384	3.1×10^{-4}	230
Hexamethylcyclotrisiloxane	D3	222	1.56	135
Octamethylcyclotetrasiloxane	D4	297	5.6×10^{-2}	176
Decamethylcyclopentasiloxane	D5	371	1.7×10^{-2}	211
Dodecamethylcyclohexasiloxane	D6	445	5.0×10^{-3}	245

damaged the generator engine moving part [13]. On the other hand, many studies have been carried out to improve the quality of indoor and outdoor air, and some of the proposed solutions are photocatalytic systems which are used for air treatment and for the development of self-cleaning materials. Once VMS are present in air, rapid catalyst deactivation could be observed and alter the efficiency of the photocatalytic system [14]. In petroleum, it has been found that the combusted form of VMS acts as a poison which causes severe catalytic deactivation by adsorption on catalyst surface in refining process [11].

In this context, their identification in different media as well as their correct quantification become essential. Their measurements require usually two steps: sampling and analysis. In addition, since VMS are present at very low concentrations, a pre-concentration step before their analysis is required.

Up to now, there is no standardized procedure for VMS quantification and results can vary considerably depending on the used methods [15].

The most widely used techniques to sample and to pre-concentrate volatile organic compounds in air and biogas are the bubbling of the gas sample through solvent filled impingers, collecting samples using either a canister or a bag, or collecting gas through adsorbent tubes. The major drawback of the bubbling of the gas sample through solvent filled impingers is the necessity to use two solvents due to the difference in solubility of TMS comparing to the other VMS. On the other hand this technique is difficult to implement for on-site measurements. Canister and bag sampling methods require a pre-concentration step before analysis and in addition when using bags some of them are permeable to certain chemicals, and losses of significant amounts of sample have been observed during long periods of storage [16]. Moreover, Tedlar bags can allow humidity to diffuse when relative humidity levels differ between inside and outside. Adsorptive enrichment on solid adsorbents is a technique used to combine pre-concentration with sampling, and it allows collection of larger volumes than with canisters [17]. However, a wide variety of organic and inorganic adsorbents are commercially available and the user is often faced with the difficulty of selecting an appropriate one. The main types of solid adsorbents used are porous organics polymers, inorganic materials and carbon adsorbents which are sub-classified into activated carbon, graphitized carbon blacks and carbon molecular sieves [18]. The major drawback of this technique is the risk of VMS losses during the sampling by incomplete adsorption of VMS.

After the sampling step, analysis can be carried out using different techniques. For example, concentration of total silicon can be determined using either atomic absorption spectrometry (ASS) or atomic emission detector (AED) [13] from absorbed VMS into appropriated solvents. Individual VMS compounds can also be determined using a separation technique such as gas chromatography coupled to a mass spectrometer (GC/MS). If solid adsorbents were used for pre-concentration, the VMS can be desorbed and analysed using a thermal desorption coupled with a Gas Chromatography and detection by Mass Spectrometry (TD-GC/MS).

In this paper, we report on the comparison of six different adsorbents, namely Carbotrap, Carbotrap C, Carbosieve SIII, Carboxen 1000, Chromosorb 106 and Tenax TA, in order to choose an appropriate adsorbent and to obtain accurate quantification of VMS.

The comparison was carried out using the breakthrough volume of the most often encountered VMS.

2. Breakthrough volume

The specific term retention volume or breakthrough volume is defined as the calculated volume of carrier gas per gram of adsorbent which causes the analyte molecules to migrate from the front of the adsorbent bed to the back at a specific temperature [19–21]. The highest breakthrough volumes would correspond to the most suitable adsorbents. Usually it is determined experimentally using two practical approaches: the elution technique and the frontal technique.

In the elution technique, the GC column is substituted by the adsorbent tube, the test substance is injected onto the adsorbent bed, and the elution chromatogram at a defined temperature is recorded. This method is based on the assumption that the analyte is present at infinite dilution and the breakthrough is only caused by a migration of the analyte through the adsorbent bed similar to gas–solid chromatography using packed columns [20]. The breakthrough value is obtained at ambient temperature by extrapolating the straight line of ln BV versus $1/T$ diagram, following the Van't Hoff equation [22].

In the frontal technique, a gas containing the studied substance is passing continuously through the adsorbent bed at a defined temperature, and the chromatogram is recorded. In this case, the breakthrough is caused by the migration of analytes and by the capacity overload at high analyte concentrations. The breakthrough volume is calculated from the reduced breakthrough time (time that marks an increase of the baseline in the frontal chromatogram). This time is defined as the intersection between the baseline and the tangent of the rising signal. In general, the frontal technique is a better simulation of the real sampling procedure but this method requires the generation of controlled gas flow for each VMS studied which is difficult to perform and time consumed compared to the elution technique [20].

While the aim of this study is to compare different adsorbents, the elution technique was used for this work.

3. Materials and methods

3.1. Chemicals

Cyclic siloxane standards (D3–D6 purity $>97\%$), linear siloxanes (L2–L5 purity $>97\%$) and TMS were provided by Aldrich and Fluka chemicals. Solid adsorbents Tenax TA (60/80 mesh), Chromosorb 106 (60/80 mesh), Carbosieve SIII (60/80 mesh), Carboxen 1000 (60/80 mesh), Carbotrap C (20/40 mesh) and Carbotrap (60/80 mesh) were obtained from Supelco. Empty standard stainless steel desorption tubes were purchased from Markes.

3.2. Tube preparation

The adsorbents used are presented in Table 2. The tubes were all packed with the same amount of adsorbent (100 mg) for the determination of Breakthrough volume. For real evaluation samples, three types of tubes were prepared: Tenax TA, Chromosorb

Table 2
Charateristics of adsorbent materials commonly used for adsorptive enrichment in ambient air analysis [16,20,28].

	Sorbent	Composition	Maximum T (°C)	Surface area ($m^2\ g^{-1}$)	Pore volume ($mL\ g^{-1}$)	
					Micro	Total
Porous organic polymers	Tenax TA	Poly (2,6-diphenyl-*p*-phenylene oxide	350	~35	0.002	0.05
	Chromosorb 106	Styrene–divinylbenzene co-polymer	250	~750	0.09	1.33
Graphitized carbon blacks	Carbotrap C	Graphitized carbon blacks	> 400	~12	_	0.02
	Carbotrap	Graphitized carbon blacks	> 400	~100	–	0.58
Carbon molecular sieves	Carbosieve SIII	Produced from polyvinylidene chloride, which eliminate hydrogen chloride at temperatures of about 180 °C	> 400	~800	0.38	0.39
	Carboxen 1000	Produced from polyvinylidene chloride, which eliminate hydrogen chloride at temperatures of about 180 °C	> 400	~1200	0.42	0.85

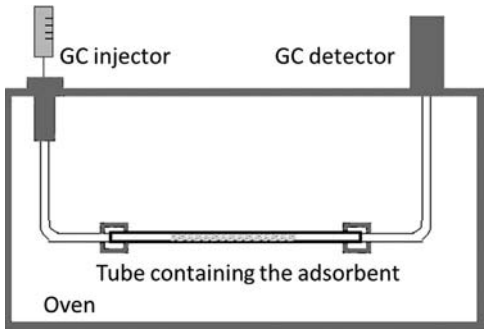

Fig. 1. Experimental apparatus for determination of VMS *BV*.

106 and multi-bed tube containing (Carbotrap C, Carbotrap and Carboxen 1000 (CC–C–C1000). The arrangement of the sorbents in the tube is carried out in such a way that the less volatile compounds are trapped on the weakest sorbent at the front end of the tube, and successively more volatile compounds are trapped by increasingly the strength of the sorbents further down the tube, with the most volatile compound trapped at the far end. The tubes were conditioned before use by heating in a stream of nitrogen (50–60 mL min^{-1}) during 3 h. Tenax TA, Carbotrap, Carbotrap C, Carbosieve SIII and Carboxen 1000 were conditioned at 300 °C while Chromosorb 106 at 250 °C. All the tubes were carefully purged and blanks were tested before use.

3.3. Apparatus

In order to accurately determine the breakthrough volumes as a function of the temperature, the system as shown in Fig. 1 was assembled. A stainless steel tube (1/4″ O.D. × 4.0 mm I.D. × 100 mm long) was packed with an accurately weighed quantity of adsorbent (100 mg) and sealed at both ends with glass wool plugs to construct the adsorbent bed. Stainless steel connecting lines (1/16″ O. D. × 0.020″ I.D.) were connected to both ends of the adsorbent. One of these lines was connected to the injection port using and the other end to the flame ionization detector of a GC "Autosystem" from Perkin Elmer. Helium was used as carrier gas, the flow rates were accurately adjusted from 10 up to 100 mL min^{-1}, and measured using a primary flow calibrator (Agilent ADM 1000). The control of adsorbent mass, carrier gas flow and oven temperature are necessary for the accurate determination of breakthrough volumes.

0.1 μL of pure VMS is vaporised in the heated injection port of the GC maintained at 200 °C. GC oven temperatures can vary from 40 to 360 °C. For each analyte, the temperature range and the flow rate were selected in order to obtain a retention time between 0.1 and 5 min. In case of Tenax TA, Carbotrap C, Carbotrap and Chromosorb 106, the Helium flow was set at 50 mL min^{-1}, for Carboxen 1000 and Carbosieve SIII, the flow rate was, respectively, adjusted at 100 and 10 mL min^{-1}. For each system studied (analyte/sorbent), BV was determinated for at least three different temperatures in order to extrapolate the BV at 25 °C, where breakthrough volume at define temperature was calculated from the measured retention time using the following relation:

$$BV(T) = \frac{(\mathrm{Tr}(T)F) - Vo}{m}$$

where Tr(T) is the retention time at temperature T, F is the flow rate, Vo is the dead volume and m is the mass of adsorbent. The dead volume was determined by injecting a non-retained analyte into the GC injection port. For most adsorbents this dead volume was about 2.0 mL. Each experiment was replicated at least three times, RSD less than 4% were always observed.

3.4. Sampling and TD-GC/MS analysis

Air were dynamically sampled by connecting tubes to air collector pump samplers SKC, the flow sampling rate was set at 30 mL min^{-1} during one hour. All samples were triplicated.

Collected air samples were then analysed using TD-GC/MS techniques. The analysis of VMS was performed by TD autosampler series 2 Ultra, thermal desorber Unity Markes, GC 6890 and MS 5973 by Agilent Technologies. The TD was programmed to desorb the tubes at 300 °C for both Tenax TA and the multi-bed tubes and at 240 °C for Chromosorb 106 assuring a total VMS desorption. The desorbed compounds from the tubes are recondensed in the cooled trap (set at −10 °C) and then the trap is desorbed by flash heating up to 320 °C and injected to GC/MS with a 10 split ratio.

Varian Select Silanes capillary column (60 m × 0.32 mm × 1.8 μm), a special column for organic silicone compounds, was used for the chromatographic separation of VMS. The oven temperature was initially set at 50 °C for 5 min, and heated at a rate of 10 °C min^{-1} to 260 °C, then maintained at this temperature during 2 min. The carrier gas flow was set at 1.4 mL min^{-1} and the GC/MS interface was set at 280 °C. The EI mass spectra was obtained for siloxanes with electron energy of 70 eV over a mass range of 30–500 amu. Acquisition mode was set to SCAN/SIM.

4. Results and discussion

4.1. Validation of our experimental set-up

Baya and Siskos have demonstrated that the breakthrough volume is independent of the sampling flow within the tested range of 50–500 mL min^{-1} [20].

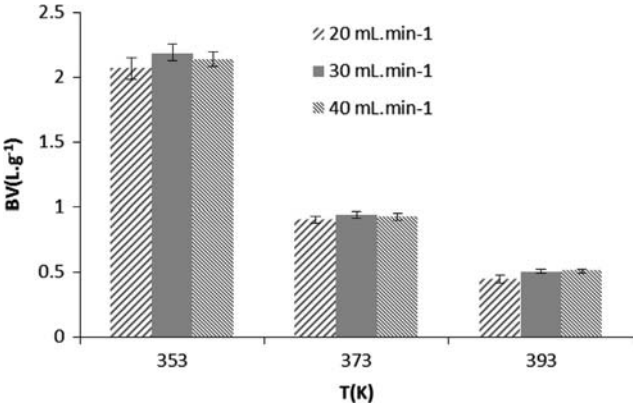

Fig. 2. Influence of the flow rate on toluene Breakthrough volume.

To confirm this result and to validate our experimental set-up, preliminary experiments were performed using toluene as model molecule and Tenax TA as model adsorbent at three different flow rates: 20, 30 and 40 mL min^{-1}. Fig. 2 shows that for three different temperatures, all BV measured were independent of the flow rates.

4.2. Determination of breakthrough volumes for VMS

Fig. 3 shows the variation of ln BV as a function of 1/T for three adsorbents (Carboxen 1000 (a), Carbotrap C (b), and Chromosorb 106 (c)) and three VMS (L2, D4, L5). By extrapolating the straight line of ln *BV* versus 1/*T*, the *BV* value at lower temperature can be determined and Table 3 gathered these values expressed in litres per gram of adsorbent at 298 K.

Results show an unexpected very low BV values for Carbosieve SIII especially for TMS and L2 as usually Carbosieve SIII is used for ultra-volatile compounds [16] while a low BV values for Carbotrap C is obtained as expected, this latter being recommended for less volatile compounds (nC_8–nC_{20}). Furthermore, results also show low *BV* values for Tenax TA especially for TMS and L2 while this latter is largely used for VMS quantification by many authors [23] leading to the conclusion that results should be underestimated when Tenax TA is used [24].

For the heaviest compounds (L3, D4–D6), it is shown that BV values increase as the compounds becomes heavier for almost all adsorbents with the exception of Carbosieve SIII and Carboxen 1000. Concerning Carboxen 1000, we were unable to determine *BV* values as no peak was observed on the chromatogram. Table 3 shows interesting high *BV* values for Chromosorb 106 for all the VMS.

As shown in Table 2, for the properties of the polymer adsorbents, the specific surface area of Chromosorb 106 is more than 20 times greater than that of Tenax TA and it is why it is generally used for atmospheres with high concentration of organic pollutants. Nevertheless, it is not suitable for accurately sampling low ppb concentrations because it can produce a high background level which makes it impractical for trace analysis [19,25]. Due to the high VMS concentration in biogas comparing to their concentration in ambient air, Chromosorb 106 seems very well adapted for sampling of biogas but not for ambient air. As a rule, the adsorption capacity of the solid sorbents increased with the increasing of their specific surface area, which could explain the highest BV values obtained for Chromosorb 106 with respect to Tenax. In the same way BV values obtained for Carbotrap are higher than Carbotrap C due its higher surface area. Usually Carbotrap is considered as a stronger adsorbent than Carbotrap C, while Carbotrap C is used for higher molecular weight compounds and they are often used together in the same tube due to their complementary properties. In addition, they are highly hydrophobic and then ideal for sampling extremely humid atmospheres such as biogas [19,26].

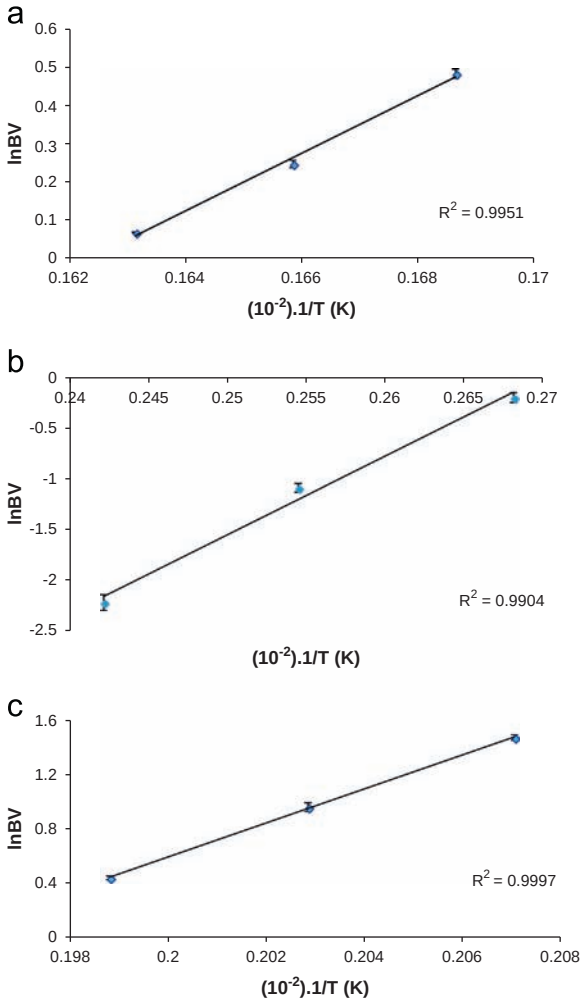

Fig. 3. Examples for ln *BV* as a function of 1/*T* for three different systems (a): L2 on Carboxen 1000, (b): D4 on Carbotrap C, (c): L5 on Chromosorb 106.

Table 3
Breakthrough volume data for VMS determinated for different sorbents.

$BV_{(L\ g^{-1})}$ at 298 K	Tenax TA	Carbotrap	CarbotrapC	Chromosorb 106	Carbosieve SIII	Carboxen 1000
TMS	0.2	0.5	0.1	39	0.03	1.2×10^4
L2	0.4	20	3	1142	0.04	49×10^4
L3	2	250	4	1.1×10^4	0.07	N.D[a]
L4	9	320	130	24×10^4	0.10	N.D
L5	80	2300	1700	470×10^4	0.26	N.D
D3	0.3	2030	15	2.4×10^4	0.06	N.D
D4	20	9800	165	14×10^4	0.07	N.D
D5	35	1.0×10^4	430	890×10^4	0.10	N.D
D6	54	1.6×10^4	1270	2000×10^4	0.11	N.D

[a] N.D.: not determined.

For the molecular sieve adsorbents, experiments showed very rapid migration of the analytes through Carbosieve SIII. Usually, retentions on carbon molecular sieves are mainly based on non-specific interactions [20], and large retention time differences between these sorbents could be observed [25].

For the two carbon molecular sieves investigated in this study, Carboxen 1000 and Carbosieve SIII, the noticeable difference of BV

values could be attributed to their different physico-chemical properties which differ mainly by their specific surface area and their porosity (Table 2). Carbosieve SIII has only micropores while Carboxen 1000 is mesoporous with a higher surface area.

For microporous sorbents, it is known that if molecules are too large to enter the pores (which is known as the "molecular sieve" effect) [25], no or a low retention between analytes and sorbent will take place, which could explain the low BV values obtained for Carbosieve III. Although Carbosieve SIII is used for light molecules, we confirm that this sorbent was really not suitable for VMS adsorption: these results were not due to experimental errors. For that, methanol was used as a volatile model compounds and result shows that Carbosieve SIII retained efficiently methanol and that the migration of methanol was slower than all the tested VMS. This could be explained by the large molecular structure of VMS that does not allow them to enter the micropores of Carbosieve SIII.

On other hand, Carboxen 1000 which is mesoporous retains efficiently VMS as shown in Table 3 for TMS and L2. Unfortunately for the heaviest compounds, the BV could not be calculated, since no peak was observed on the chromatogram even at high GC oven temperature (360 °C) which was attributed to an irreversible adsorption. That is why Carboxen 1000 generally combined with adsorbents having lower adsorption capacity, so as to maintain less volatile compounds from being irreversibly retained in the molecular sieve (Carboxen 1000) [16].

The specific surface area of adsorbents plays also an important role in adsorption. Carboxen 1000 has a higher surface area than Carbosieve SIII, this may help Carboxen 1000 to adsorb more VMS than Carbosieve SIII [27].

Due the difference in volatility between VMS, it is difficult to find an adsorbent to adsorb all VMS. Multi-bed tube could solve this problem. Tubes containing beds of different sorbents have become more and more used. The arrangement of the sorbents tubes is done in such a way that the less volatile compounds are trapped on the weakest sorbent at the front end of the tube, and successively more volatile compounds are trapped by increasingly the strength of the sorbents further down the tube, with the most volatile compound trapped at the far end [25].

In this context, the most commonly multi-bed tube used consists in the association of Carbotrap C, Carbotrap and Carbosieve SIII [20]. As we have shown that Carbosieve SIII was not suitable for VMS analysis, we propose rather the combination of Carbotrap C, Carbotrap and Carboxen 1000 in this order of sampling. Carboxen 1000 is used to adsorb the lightest VMS L2 and TMS, Carbotrap for D3, L3 and Carbotrap C for the others VMS. On the other hand Chromosorb 106 could be used to adsorb VMS at high concentration. The association of Chromosorb 106 to other adsorbents such as Carbotrap shows its limits due to the difference in the maximum desorption temperature of Chromosorb 106 as shown in Table 2, comparing to the other during analysis. Concerning the three adsorbents proposed the maximum desorption temperature is the same.

4.3. Evaluation of real samples

To confirm the results, VMS were measured in indoor air using three types of tubes filled with solid sorbents tested in this work which were: Tenax TA, Chromosorb 106 and an association of Carbotrap C, Carbotrap and Carboxen 1000. Table 4 shows similar results for Chromosorb 106 and the multi-bed tube containing Carboxen 1000 for all VMS, while an underestimation of concentration for the lightest VMS was observed when Tenax TA is used. For these samples, the concentrations of L2 and TMS are more than five times lower with Tenax TA than the ones with Chromosorb 106 and the multi-bed tube containing Carboxen 1000 are used. This result is an agreement with the low breakthrough volume data obtained for TMS and L2 with Tenax TA.

Table 4
VMS concentrations in indoor air.

Concentration μg m^{-3}	Chromosorb 106	CC–C–C1000	Tenax TA
TMS	2.5 ± 0.4	2.3 ± 0.3	0.3 ± 0.2
L2	1.6 ± 0.2	1.3 ± 0.2	0.25 ± 0.08
L3	< 0.06	< 0.06	< 0.06
D4	3 ± 0.3	3.2 ± 0.3	3 ± 0.3
L4	< 0.06	< 0.06	< 0.06
D5	16 ± 2	16 ± 2	15 ± 3
L5	< 0.06	< 0.06	< 0.06
D6	0.83 ± 0.08	0.79 ± 0.09	0.81 ± 0.08

5. Conclusion

The determination of *BV* for different sorbents applied to the main VMS allow us to select suitable adsorbent for gas sampling of VMS either in biogas or in ambient air.

It has been found that Tenax TA present low breakthrough values for almost all compounds suggesting that it is not a suitable adsorbent for VMS. Same results are obtained with Carbosieve SIII.

On contrary, Chromosorb 106, and the association of Carbotrap C, Carbotrap and Carboxen 1000 give better results. Hence, if an exhaustive analysis of ambient air or biogas would be done, sorbent tubes that assure a complete gathering of VMS without loss of sample would be more appropriate, such as a multi-adsorbent bed (Carbotrap C, Carbotrap and Carboxen 1000) or Chromosorb 106.

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